Absorption of Water Vapor into LiBr Solutions with 2-Ethyl-1-Hexanol

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Absorption of water vapor into a liquid falling film of 50 to 63% lithium-bromide solution is a part of a typical absorption refrigeration cycle. The heat- and mass-transfer rate of the absorption step is often an important factor in the economic design. Significant enhancements in the heat- and mass-transfer rate can be obtained by adding small amounts of surface active agents such as 2-ethyl-hexanol, as shown by Chi et al. (1971).

In the absence of mass transfer and surface active agents and for film Reynolds numbers in the range 20 to 100, falling films are laminar or wavy depending upon the experimental initial conditions. Mass transfer from the gas phase to the liquid phase without surface active agents gives more stable surface conditions, and surface active agents without mass transfer also stabilize the film. However, when both mass transfer and surface active agents are present, the surface tension gradients due to concentration differences can lead to instability, as explained by Sternling and Scriven (1959). In spite of this general understanding of the mechanism, in the system with aqueous lithium bromide and 2-ethyl-1-hexanol the exact role of surface tension gradients due to temperature, concentration of solute, and concentration of surfactant are not well documented.

Most prior experimental work involved absorption to a stagnant pool (Kashiwagi, 1988; Hozawa et al., 1991) where increased mass-transfer rates of factors of two to three were observed. Consenza and Vliet (1990) found a factor of at least two to increase with surface active agents in horizontal tube falling films, and Hihara and Saito (1993) found similar increases in a vertical falling film. Both the falling film experiments were limited to concentrations of 2-ethyl-1-hexanol over 50 ppm by weight, and both observed longitudinal waves during the experiment which were not present without the surfactant.

A linear stability analysis for a jet (which is equivalent to a stagnant pool) under adiabatic conditions was presented by Ji et al. (1993). Based on this theoretical study, the critical Marangoni number (Ma) for the onset of the instability should be of the order 10^8. Using the values of surface tension gradients from Kim et al. (1994), the mass-transfer enhancement in falling films of 50–60% lithium-bromide with 2-ethyl-1-hexanol should be evident at surfactant concentrations above approximately 5 ppm. Experiments to verify the onset hypothesis and the effect of other variables on the mass-transfer coefficient are the major objectives of this work.

Experimental Studies

The experimental equipment and details of the experimental method are described by Kim (1992). The absorber consists of two concentric tubes, an inner stainless steel tube of OD 38.1 mm and length 1.83 m and an outer pyrex tube of ID 148 mm and length 1.22 m. The lithium-bromide solution is fed by gravity into a distributor and then falls down the outside of the steel tube. The apparatus operates in a once through mode. Water vapor from an evaporator flows countercurrently from its introduction at the bottom of the space between the tubes, and cooling water flows in the inside of the inner tube. The system between the tubes is under vacuum, and nonabsorbable concentration is controlled and measured as described by Kim (1992). The average nonabsorbable concentration was kept at less than 2%. Flow rates, inlet and outlet concentrations, and temperatures were measured for 50 and 60 wt. % lithium-bromide with 0 to 200 ppm of 2-ethyl-1-hexanol. Lithium hydroxide was added to raise the pH to approximately 10 to inhibit corrosion. The mass-transfer coefficient was calculated using the water mass-transfer rate determined from the liquid flow rate at the top of the absorber, and the total flow at the bottom. The driving force was the log mean concentration difference between the surface concentration corresponding to the temperature and pressure assuming only water in the gas phase and the bulk concentration.

The 0% additive case was studied extensively to determine the influence of nonabsorbables on the results and to justify

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the use of mass diffusivities measured by Kashiwagi (1984). The results showed that a 1% average nonabsorbable concentration meant that there was a 10% concentration of nonabsorbables at the surface at the bottom of the apparatus which led to a 50% reduction in mass transfer for the wavy films under typical experimental conditions. For both 50 and 60% lithium-bromide solutions, the Sherwood number did not depend on the mass-transfer driving force.

In the additive study we closely matched the driving forces (partial pressure differences) for 50 and 60% and varied the concentration of additive. For the base case with 50% lithium bromide solution, the absorber length was 0.85 m; feed temperature was 30°C; pressure was 11.3 torr; cooling water temperature was 20°C; and the film Reynolds number was 75. The corresponding parameters for 60% lithium bromide were 40°C feed temperature, 7.6 torr absorber pressure, 30°C cooling water, and a film Reynolds number of 60. To investigate other aspects of the absorption, the absorber length, the inlet temperature, the cooling water temperature, the nonabsorbable concentration, and the pressure were varied. In this way the effect of the driving force which controls the magnitude of the Marangoni number could be investigated.

A complete list of the database sources is given by Kim (1992). Surface tension gradients due to lithium-bromide concentration, surfactant concentration, and temperature were calculated from measurements of surface tension with the Du Nouy ring method and reported in Kim et al. (1994). In addition a few measurements of surface tension were made by Janule (1992) using the maximum bubble pressure technique. The bubble is created with a fresh surface, and an estimate of the time constant for formation of an equilibrium surface can be found from the measurements as a function of time. For 50% lithium-bromide solution, the time constant is of the order of 10 s and for 60% lithium bromide the time constant is several hundred s, both for 200 ppm 2-ethyl-1-hexanol.

In lithium-bromide solutions the lithium ion has four molecules of water in the first coordination ring (Valeev et al., 1993). For solutions with lithium-bromide concentrations greater than about 56% by weight, there are less than four water molecules per lithium ion. The movement of water in lithium-bromide solutions is somewhat restricted but the diffusivity of water in 50% solution is 1.223×10^{-9} square meters per second and in 60% solution 0.89×10^{-9} square meters per second, only about a 40% difference. The diffusivity of 2-ethyl-1-hexanol may have a much greater difference to obtain the observed dynamic surface tension results. There are three Marangoni numbers which arise from the surface tension gradients at the boundary

$$Ma_{\mathrm{LiBr}} = -\left(\frac{\partial\sigma}{\partial C_{\mathrm{LiBr}}}\right)\frac{\Delta C_{\mathrm{LiBr}} L_{\mathrm{ch}}}{\mu D} \tag{1}$$

$$Ma_{\mathrm{add}} = -\left(\frac{\partial\sigma}{\partial C_{\mathrm{add}}}\right)\frac{\Delta C_{\mathrm{add}} L_{\mathrm{ch}}}{\mu D_{\mathrm{add}}} \tag{2}$$

$$Ma_{T} = -\left(\frac{\partial\sigma}{\partial T}\right)\frac{\Delta T L_{\mathrm{ch}}}{\mu\alpha} \tag{3}$$

The overall Marangoni number is the sum of these three. The diffusivity of surfactant (additive) is assumed to be the same as that of water in the calculations that follow. All properties are evaluated at the average temperature of the falling film.

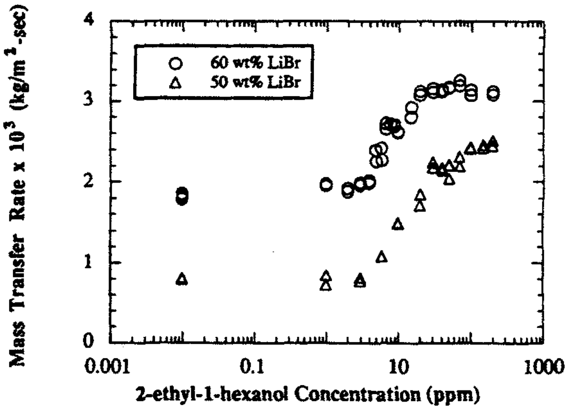


Figure 1. Additive concentration effect on mass-transfer rate.

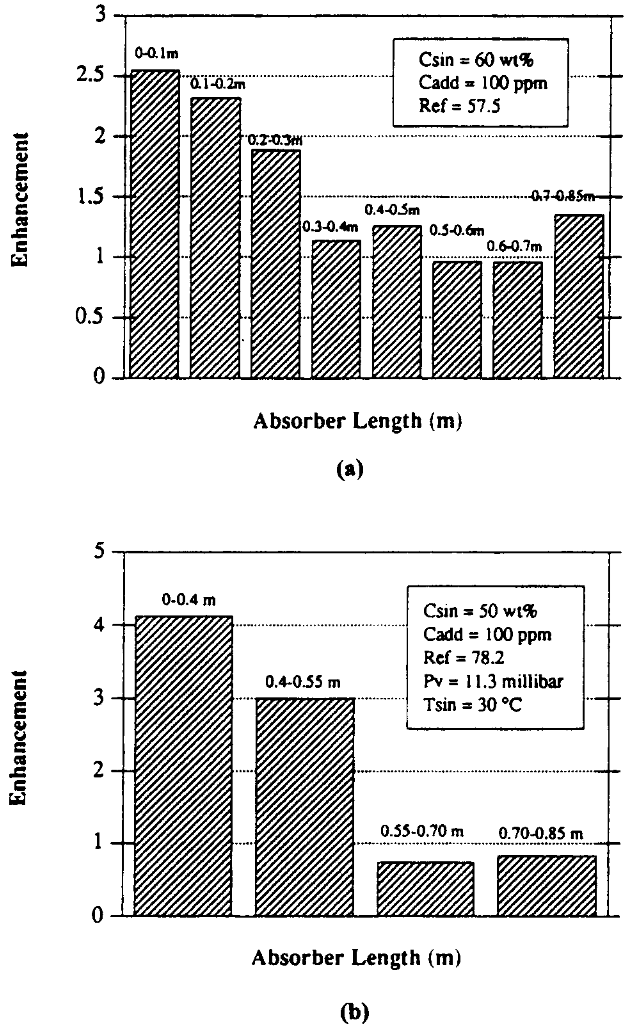
For 50% LiBr: C_{add} = 0–200 ppm, T_{sin} = 30.1°C, T_{cin} = 20.0°C, P_v = 8.5 Torr, Re_f = 75.8, L = 85 cm; for 60% LiBr: C_{add} = 0–200 ppm, T_{sin} = 40.0°C, T_{cin} = 30.0°C, P_v = 7.6 Torr, Re_f = 69.3, L = 85 cm.

Results and Discussion

When the additive concentration was varied from one to 200 ppm and all other variables described by the base parameters, the mass-transfer rate began to increase at two to six ppm as shown in Figure 1. The mass-transfer rate reached a maximum value near 30 ppm and was constant up to 200 ppm. The enhancement of mass transfer was higher for 50% lithium-bromide than for the 60% solution. Visual observations of the flow patterns revealed turbulence and longitudinal waves similar to that observed by Hirata and Saito, however, only for about half of the length of the absorber (Hirata and Saito used an absorber of length 0.3 m and did not report any change in flow pattern along the length).

From the surface tension measurements, the solubility of 2-ethyl-1-hexanol in 50% lithium bromide solution is about 200 ppm and in 60% lithium bromide is about 50 ppm. At higher concentrations a second surfactant phase is formed [Kashiwagi (1985) shows photos of this second phase on the surface for 1-octanol]. The results of this work on absorption indicate that mass-transfer enhancement does not depend on the existence of a second phase, as suggested by Kashiwagi (1985) and Morioka and Kiyota (1990). It appears that the onset of enhancement occurs when the surface tension of the lithium bromide solution plus additive equals that of pure water or when the Marangoni number exceeds the critical value, as will be shown later.

The absorber length could be varied from 0.1 to 0.85 m by changing the level of the solution collector. With fixed additive concentration of 100 ppm, the length was varied when all other parameters were maintained the same as the base case. The results are presented in Figures 2a and 2b where the mass-transfer enhancement is defined as the ratio of the mass-transfer rate with additive to the mass-transfer rate without additive. These results show larger enhancements at shorter absorber lengths, and no enhancement beyond 0.3 m



(a)

(b)

Figure 2. Effect of absorber length on mass-transfer enhancement.

(a) 60% LiBr; (b) 50% LiBr.

for the 60% solution and beyond 0.55 m for the 50% solution. There is a decrease in mass transfer beyond 0.55 m for the 50% solution and beyond 0.3 m for the 60% solution, but not a complete shutdown of mass transfer. For the 50% solution, this indicates that there is more nonabsorbable gas at the surface than when no surfactant is present. The 60% solution does not appear to build up as much nonabsorbable gas at the interface down the absorber, because the mass-transfer rate is less than for the 50% solution.

Clearly, the Marangoni number must be below the critical for the enhancement to end, and we propose that the reason for this is the effect of the dynamic surface tension. Similar decays of mass transfer in chemical absorption has been reported by Imaishi and Fuginawa (1980) and in liquid-liquid extraction by Javed et al. (1989). There is not enough time for the surface to be exposed to the vapor phase for an equilibrium surface to be established, and when there is turbulence the liquid surface in contact with the vapor is rapidly replenished with bulk liquid. In the upper part of the absorber the 50% solution starts with more surfactant at the surface. Measurements of the surfactant concentration at the base of the absorber show no change in the bulk concentration compared to the feed tank.

To study the effect of Marangoni number the absorber length was set at 0.4 m, the 2-ethyl-1-hexanol was held at 100 ppm, and factors which affect the driving potential were changed (inlet solution temperature, inlet cooling water temperature, absorber pressure, and inlet solution concentration of lithium-bromide). When there is no surfactant present, the results are consistent with about 10% nonabsorbables concentration at the surface at the bottom of the absorber for the base case. When the surfactant is present, the increased mixing leads to a higher mass-transfer rate and thus to higher nonabsorbable concentrations at the same point in the absorber compared to without surfactant. When the absorber pressure is 10 millibars, the mass-transfer enhancement for 60% LiBr with additive is a factor of 2.3 and when the pressure is raised to 13 millibars, the enhancement increased to 3.0. This experiment proves that the Marangoni number influence on the mass transfer is much greater than the effect of nonabsorbables. Therefore, the experiments can be used to demonstrate the effect of Marangoni number and the nonabsorbable effects can be considered as constant.

It is difficult to determine the true Marangoni number for these experiments since an equilibrium surface is never present. However, we can use the equilibrium surface tension results of Kim et al. (1994) to get information on the onset of the instability and on the dimensionless mass-transfer rate dependence on the equilibrium Marangoni number. The Marangoni numbers defined in Eqs. 1 to 3 as functions of concentration are shown in Figures 3 and 4 for 60 and 50% lithium-bromide, respectively. The change in overall Marangoni number from negative to positive corresponds closely to the onset of mass-transfer enhancement. The Marangoni number due to temperature gradient is small compared to the Marangoni numbers due to lithium-bromide and 2-ethyl-1-hexanol concentration gradients. The magnitude of the Marangoni number at onset corresponds to the theoretical calculations of Ji et al. (1993). The 60% solution would be predicted to have an onset at a lower surfactant concentration based on the calculated equilibrium Marangoni number, and this is also observed in Figure 1. The Marangoni

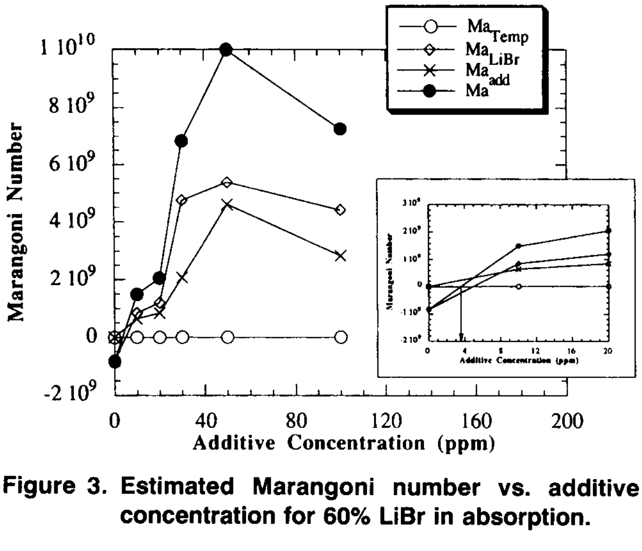


Figure 3. Estimated Marangoni number vs. additive concentration for 60% LiBr in absorption.

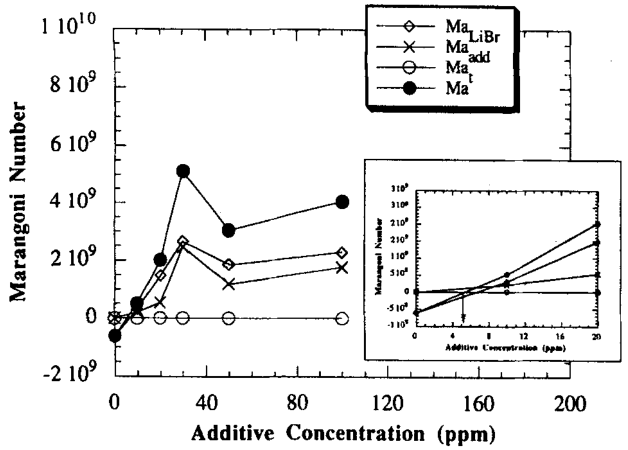


Figure 4. Estimated Marangoni number vs. additive concentration for 50% LiBr in absorption.

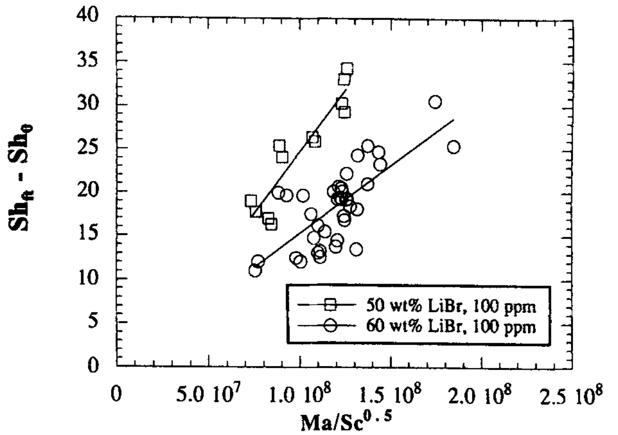


Figure 5. Mass-transfer correlation between Sh_{ft} and Ma.

The lines are least-squares fit to the data.

numbers reach a constant maximum at approximately 30 ppm, and there is little change at higher concentrations. This again is consistent with the mass-transfer enhancement observations. The 60% solution does have a higher Marangoni number at the maximum than the 50% solution, but the 50% solution has the higher mass-transfer enhancement. This implies that the true concentration at the surface does not correspond to the equilibrium value.

To determine the effect of Marangoni number on the results of the entire series of experiments, a linear correlation with Marangoni number of the form suggested by Golovin (1992) and Rabinovich (1992) based on turbulent scaling would be

$$Sh_{ft} = Sh_0 + b^2(Ma - Ma_{on})Sc^{-1/2} \qquad (4)$$

where the subscript ft indicates the enhanced dimensionless group, the subscript on indicates onset and the subscript 0 indicates the laminar flow dimensionless group for short contact time. The parameter b includes the effects of absorber length and dynamic surface tension. The 60% data and some 50% lithium-bromide with 100 ppm 2-ethyl-1-hexanol for a 0.40 m length absorber are shown in Figure 5 (in this case, the mean film thickness was used for a length scale). For the 50% experiments, only the absorber pressure was changed to obtain the variations in Marangoni number. The overall equilibrium Marangoni number with no correction applied to account for nonabsorbables is used in Figure 5. Within experimental error, each concentration is consistent with a linear dependence on Marangoni number. The two curves extrapolate to an onset Marangoni number in the 10^7 to 10^8 range; however, the curves do not collapse to a single one indicating that there is some fundamental difference in the two cases. Possible explanations are nonabsorbable concentration, errors in the diffusivities used in the analysis, and the dynamic surface tension effects. The nonabsorbable concentration effect cannot account for the difference in the Sherwood number vs. Marangoni number plots for the two lithium bromide concentrations, because the correction would bring the curves further apart. Without the correction, the driving force is almost constant for the experimental data sets and with a nonabsorbable correction the Marangoni number for 50% would be corrected toward lower Marangoni numbers more than that for the 60% solution. A lower diffusivity for water in the 60% solution must be rejected, because the results of mass-transfer experiments without 2-ethyl-1-hexanol could not be correlated (Kim, 1992). We conclude that the explanation must be that the true surface concentrations of 2-ethyl-1-hexanol must be different than the equilibrium values, because the surface exposure time is short for a falling film experiment.

Conclusions

Extensive experimental studies of absorption of water vapor to falling films of lithium-bromide solution with small amounts of 2-ethyl-1-hexanol show that a critical Marangoni number can be found for the onset of mass-transfer enhancement (instability). This critical Marangoni number was the same when the surfactant concentration was varied or when the average overall liquid driving force was varied to obtain a change in Marangoni number.

Although both 50 and 60% lithium bromide solutions showed a linear dependence of Sherwood number on Marangoni number, the two lines fit to the data had different slopes and did not collapse to a single line. This anomalous behavior is explained by the effect of dynamic surface tension differences between the two cases. Other explanations do not fit all experimental observations. The difference between 50 and 60% lithium-bromide solutions may be due to the coordination of lithium ion with four molecules of water. A 50% solution will have some free water, but there is no free water in a 60% solution. Then diffusion of the 2-ethyl-1-hexonal molecule from the bulk to the vapor-liquid surface is restricted for the 60% case compared to the 50% case.

The linear dependence of the Sherwood number on Marangoni number also corresponds to a turbulent falling film and not a wavy mode, which has been observed in temperature driven Marangoni instabilities. Such modes would give a Marangoni number to the one-half power dependence (Golovin, 1992). They are not observed here possibly because the Marangoni number is very large for even a small absorbent concentration difference when the dominant surface tension gradient is due to the change with lithium-bromide concentration, or the falling film instability may always lead to turbulent flow.

Acknowledgment

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Notation

C = concentration
D = mass diffusivity
g = gravitational acceleration
h_m = mass-transfer coefficient, mass-transfer rate/(area × average concentration difference)
L = absorber length
L_{ch} = characteristic length $= (\nu^2/g)^{1/3}$
Ma = Marangoni number
P = pressure
Re = Reynolds number, $4\Gamma/\mu$
Sc = Schmidt number $= \nu/D$
Sh = Sherwood number $= h_m L_{ch}/D$
T = temperature

Greek letters

α = thermal diffusivity
Γ = liquid mass flow rate per perimeter
Δ = difference
μ = dynamic viscosity
ν = kinematic viscosity
σ = surface tension

Subscripts

add = additive or surface active agent
cin = cooling water inlet
f = liquid film
sin = solution inlet
T = temperature
v = vapor

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